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3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

CAMBRIDGE DISPLAY TECHNOLOGY LTD
181a Huntingdon Road
Cambridge, CB3 ODJ
UNITED KINGDOM

Patents ADP number *(if you know it)*

06166L1001

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

MATERIALS FOR POLYMER ELECTROLUMINESCENT DEVICES

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

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1255003

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Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*
UK	9722102.2	21-10-97

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Number of earlier application	Date of filing *(day / month / year)*

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11. I/We request the grant of a patent on the basis of this application.

Signature Page White & Farrer Date 08.07.98

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Dr. CHRIS HILL - 0171 831 7929

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References Cited

U.S. PATENT DOCUMENTS

3,401,152/1968 Wessling *et al.*

5,558,904-A/ Hsieh *et al.*

OTHER PUBLICATIONS

J. H. Burroughes et al., *Nature*, 1990, **365**, 47.

H. G. Gilch et al., *J. Polym. Sci. 1-A*, 1966, **4**, 1337.

B. R. Hsieh et al., *Adv. Mater.*, 1995, **7**, 36.

H. Antoniadis et al., *Polym. Adv. Tech.*, 1997, **8**, 392

SUMMARY

Organic materials-based light-emitting diodes (LEDs) are disclosed in which the use of a layer of emissive polymer enables efficient devices to be constructed using aluminium or calcium cathodes. The polymer, a poly(1,4-phenylene vinylene) (PPV) derivative, carries substituents on the 2,3-positions of the phenylene ring. This substitution pattern produces a blue-shifted emission and high PL and EL device efficiencies. The polymerisation route is simple, the polymer is soluble, and displays good film forming properties with high photoluminescence in the solid state.

MATERIALS FOR POLYMER ELECTROLUMINESCENT DEVICES

FIELD OF INVENTION

The present invention is directed to polymer-based light-emitting diodes (LEDs), in particular to the synthesis and fabrication of novel 2,3-disubstituted poly(1,4-phenylene vinylene) derivatives based LEDs.

BACKGROUND OF INVENTION

The potentially high photoluminescent quantum yield in organic semiconductors has made light emission through charge injection under an applied field (electroluminescence) a reality. This has thus resulted in the use of organic materials for LEDs, with the use of polymers as an advantage over smaller organic compounds in improving structural stability and processibility of the organic layers.

The first polymer-based LEDs consisted of an emissive layer of poly(1,4-phenylene vinylene) (PPV) sandwiched between indium tin oxide (ITO) as the hole injection electrode and aluminium or calcium as the electron-injecting electrode (Burroughes *et al.*, *Nature*, 1990, **347**, 539). This has been followed in other polymers for LED applications, with emphasis on the tuning of the emission colour by controlling the substitution pattern and the effective conjugation length in the polymer.

The route used for the synthesis of PPVs for LEDs has been predominantly the Wessling sulfonium salt precursor route (U.S. Pat. 3,401,152/1968 Wessling *et al.*) while another important method by Gilch (Gilch *et al.*, *J. Polym. Sci. 1-A*, 1966, **4**, 1337), involved dehydrohalogenation of bis(halomethyl)benzene monomers with excess potassium t-butoxide to directly obtain the conjugated polymer. This protocol has been applied to the red emissive poly(2,5-dialkoxy-1,4-phenylene vinylene)s which have a typical Absolute PL efficiency of *ca.* 15-20%. A modification of this route by Swatos and Gordon, the chloro-precursor route, used one equivalent of base to form the chloro-substituted soluble precursor polymer which was then thermally converted to form the fully conjugated polymer [Swatos and Gordon, *Polym. Prepr.*, 1990, **31 (1)**, 505]. This route has since been used by various groups to make alkyl-, aryl- and alkoxy-substituted PPVs (Hsieh *et al.*, *Adv. Mater.*, 1995, **7**, 36 & *Polym. Adv. Tech.*, 1997, **8**, 392; Sarnecki et al., *Synth. Met.*, 1995, **69**, 545).

SUMMARY OF THE INVENTION

The present invention describes the surprising discovery of efficient (relatively) blue-shifted emission from 2,3-disubstituted PPV-based materials and their use in LEDs. This invention explores the unconventional substitution patterns at the 2,3-positions on the aryl ring as opposed to the standard 2,5-disubstituted PPVs and thus provides a means of tuning the colour of emission. In addition, the present invention provides a luminescent polymer that is both soluble and directly obtainable by the Gilch route. The invention refers to the synthesis of novel materials and their application in organic LEDs.

DESCRIPTION OF THE INVENTION

The electroluminescent (EL) device according to the present invention are injection-type diodes in which at least one active (EL) and one or more charge transport layers (if desired) are sandwiched between two different conducting layers (electrodes). One electrode is a hole-injecting translucent or transparent electrode while the other is an electron-injecting electrode. The electrodes are electrically connected to each other and to a source of current to create a complete circuit. Improved efficiencies may be obtained using bilayer devices with PPV or hole transporting layers e.g. poly(vinyl carbazole) (PVK).

This invention refers in one specific embodiment to the synthesis of the polymer, poly[(2,3-dibutoxy)-1,4-poly(phenylene vinylene)] **1** using the dehydrohalogenation method with base (potassium tert-butoxide). The resultant polymer has high molecular weight and its alkyl chains enable solubility in organic solvents such as chloroform and tetrachoroethane. Surprisingly, the solid film fluoresces with high efficiency (absolute PL efficiency 40%) in the yellow green region despite having alkoxy substituents. In a

further example the polymer **2** was synthesised. In addition to its emissive properties in PL and EL devices it has the potential to serve as a component of a sensor owing to its affinity for metal ions.

In a further embodiment, the fluorescent oligomer **9** has been synthesised using the Wadsworth-Emmons reaction of a dialkoxybenzyl bisphosphonate **8** and dialkoxy-benzaldehyde **7**. Evidence for the origin of the blue shifted emission and possible high fluorescence efficiency comes from the single crystal X-ray study of **9** which shows that the aromatic rings are twisted in a notable manner, thus resulting in the disruption of the effective conjugation length of the polymer backbone. The localisation of the conjugation could also be due to the cisoid-like disposition of the styryl substituents in **9**. (see Figure 5 later)

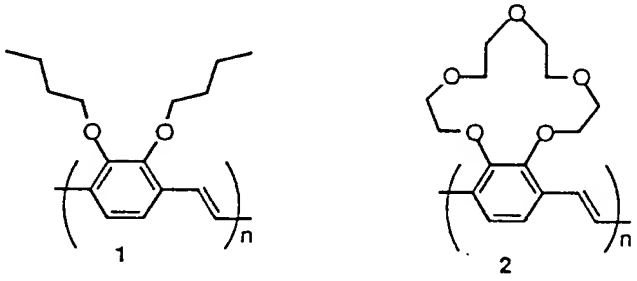
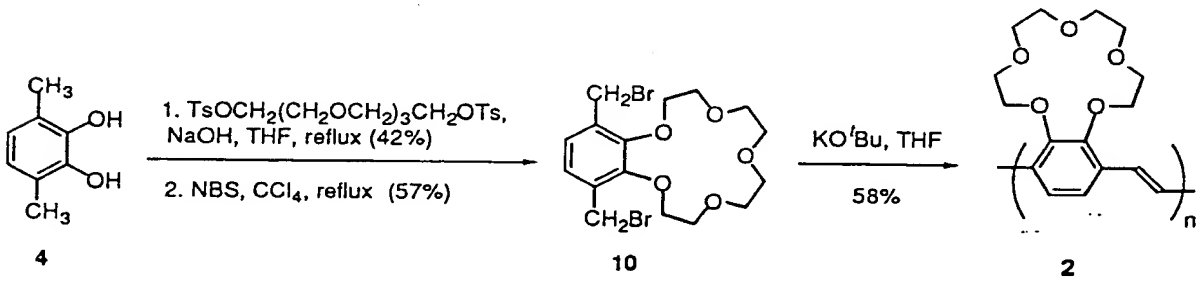


Figure 1 Structure of the poly[(2,3-dibutoxy)-1,4-poly(phenylene vinylene)] (PDB-PPV) **1** and the crown ether analogue **2**

The crown ether analogue **2** is also fluorescent. It is prepared as shown in Figure 2 below.



4 **10** **2**

Figure 2 Preparation of 15C5 crown ether **2**

As the polymer **2** is also luminescent and can be advantageous in lighty emitting electrochemical devices and other devices where chelation of various metal ions, preferably lithium, can lead to ionically doped materials fabricated out of a homogeneous phase rather than from a blend of more than one polymer which may phase-separate. Such doping can lead to reduced barriers for charge injection into the emissive layers. Statistical copolymers derived from dehydrohalogenation condensation polymerisation of the building block **10** with either the DMOS precursor **11** or the dibutoxy precursor **6** afford efficient devices (Figure 3). The ratio of *m*:*n* may range from 10:1 to 1:10, preferably *ca.* 1:1.

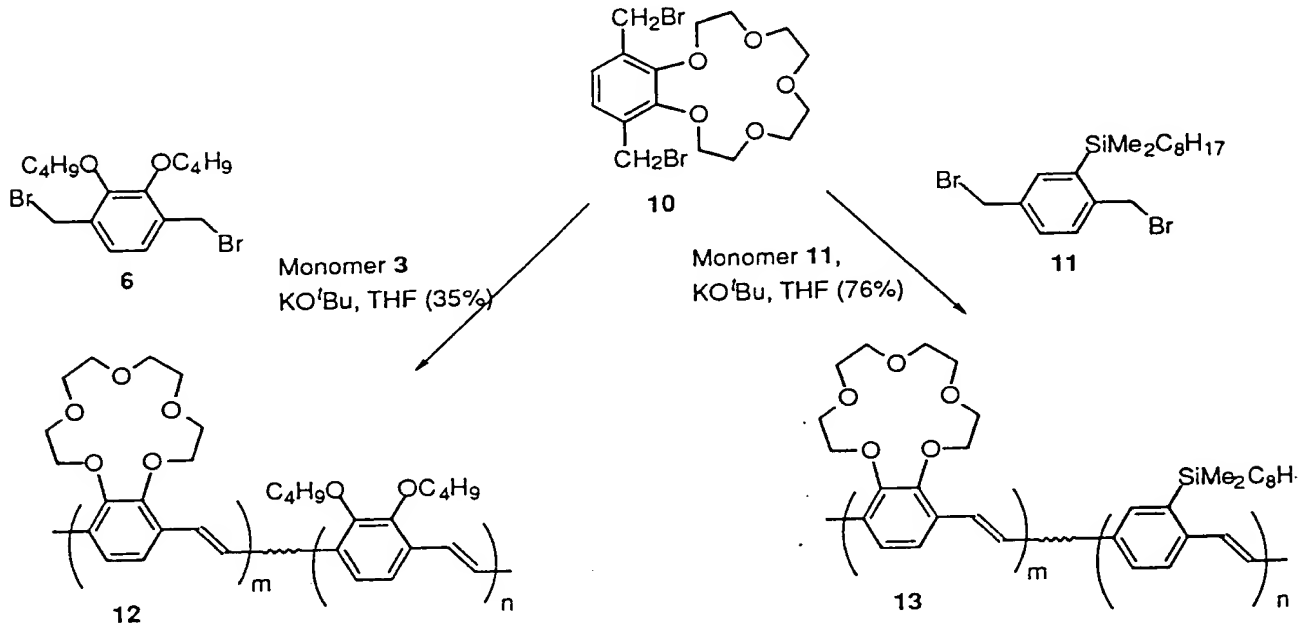


Figure 3 Statistical copolymers **12** and **13**

Two layer devices were fabricated using **1** as follows. A layer of a PPV precursor polymer, fabricated according to the sulfonium salt decomposition method described in U.S. Patent No. 3,401,152/1968, is spin-coated onto a glass plate coated with ITO and thermally converted to PPV. In the other type of bilayer device, a transporting layer of PVK is spin-coated from solution directly onto ITO.

Next, a layer of the polymer poly[(2,3-dibutoxy)-1,4-poly(phenylene vinylene)] (PDB-PPV) **1** is spin-coated onto the

PPV layer followed by a layer of aluminium or calcium deposited under vacuum onto the polymer layer. Contacts are attached and a connection is made to a DC power source. Application of a forward bias voltage results in emission of yellow-green light with emission maximum at about 2.3 eV (*ca.* 550 nm), and a brightness in excess of 4,500 cd/m^2. Internal efficiencies of about 1.5% were observed with calcium as the cathode.

Based on the illustrative examples it is evident that highly efficient devices can be obtained by the dehydrohalogenation route to prepare 2,3-disubstituted-1,4-arylenevinylene polymers from monomers carrying aryl, heteroaryl, alkyl, and branched alkyl substituents linked either by carbon or heteroatom linkages to the aromatic backbone of the polymer. A preferred substituent is the butyloxy and other preferred substituents are ethylhexyl(oxy) and 3',7'-dimethyloctyl(oxy). Other preferred carbon chains up to ten carbon atoms and carrying branching substituents are advantageous. Similar effects are expected with any conjugated polymer (poly fluorene, polythienylene, polyphenylene, poly[thienylene-co-phenylene] etc) or a copolymer arising from a fluorescent unit carrying a distyrylbenzene fragment with the 2,3-disubstitution at least on the central aromatic ring.

Previous examples with a 2,3-diphenyl substitution would not be expected to demonstrate these novel features based on the reports of H. Antoniadis et al., *Polym. Adv. Tech.*, 1997, **8**, 392 owing to the need to use the precursor route to generate the final polymer.

EXAMPLES

A method of preparing the conjugated polymer PDB-PPV **1** involves the preparation of the monomer of formula Br-CH_2-Ar-CH_2-Br which is subjected to polymerisation with six equivalents of base, potassium tert-butoxide preferably in THF or dioxane to give the desired polymer which is soluble in organic solvents such as chloroform and tetrachloroethane.

The synthesis of the polymer is shown in the following scheme (Fig **4**):

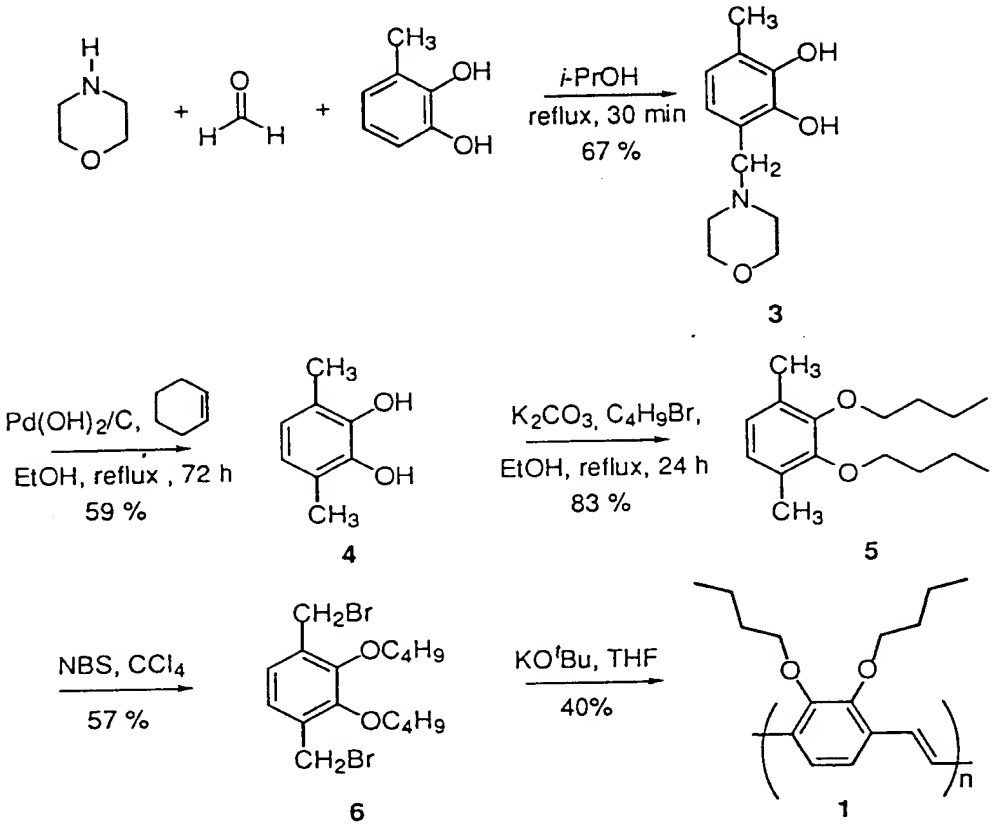


Figure 4 Preparation of PDB PPV **1**

EXAMPLE 1 Preparation of monomer **6**

Methyl catechol derivative **3** was synthesised by performing a Mannich reaction with formaldehyde and morpholine following the method described by Helgeson et al. (*J. Am. Chem. Soc.*, 1977, **99**, 6411). Transfer hydrogenation using palladium hydroxide on carbon to remove the morpholine group in the presence of a hydrogen donor (Hanessian et al., *Synthesis*, 1981, **118**, 396) subsequently produced the dimethyl catechol **4** in reasonable yield (59%). *O*-alkylation was then carried out using copious excess of potassium carbonate and dibutyl bromide to give a reasonably high yield (83%) dialkoxy-xylene **5**. Radical bromination of the xylene with slight excess of *N*-bromosuccinimide in carbon tetrachloride as given in Gruter et

al., *J. Org. Chem..*, **59**, 4473 gave the monomer **6** in comparatively high yield (57%).

EXAMPLE 2 Preparation of polymer **1**

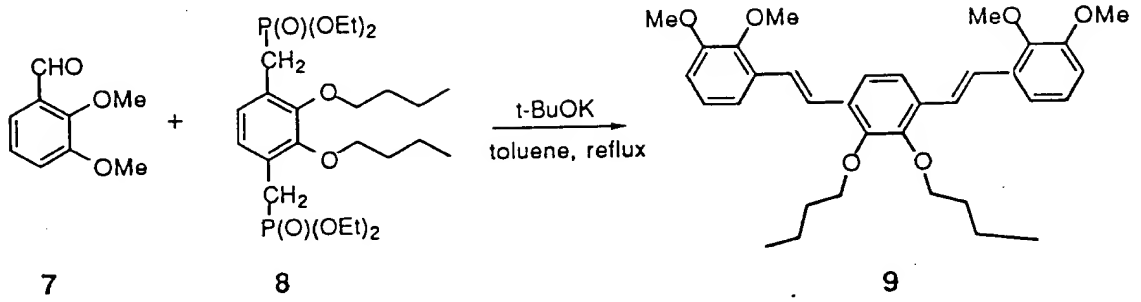
A degassed solution of the monomer **6** (0.24 g, 0.6 mmol) in dry THF (16 cm^3) was added slowly over 20 min to a degassed solution of potassium tert-butoxide (0.41 g, 3.6 mmol) in dry THF (16 cm^3) at room temperature. The reaction mixture was stirred at room temperature under nitrogen for 18 h, after which it was poured into methanol. The resultant yellow precipitate was collected by filtration and reprecipitated into methanol. The polymer **(1)** was collected as a bright yellow solid (60 mg, 40 %). Found: C, 76.6; H, 9.1; Br, 0 ; $[C_{16}H_{22}O_2]_n$ requires C, 78.0; H, 9.0; Br, 0 %). GPC assay in $CHCl_3$ revealed M_W 2,120,000, M_n 361,000 and M_W/M_n 5.9; $\lambda_{max}(CHCl_3)$/nm 444; λ_{max}(film)/nm 450; PL emission (max)/nm 551 (2.25 eV); PL efficiency 40 %; EL emission (max)/eV 2.28.

EXAMPLE 3 Fabrication of a 2-layer LED with polymer **1**

A film of PPV (*ca.* 100 nm in thickness) was prepared by spin-coating a solution of a sulfonium precursor polymer onto a glass plate coated with indium tin oxide and thermally converting the film at 230 °C in vacuum for 6h. A 1% (w/v) solution of the polymer **1** in chloroform was spin-coated on top of the converted PPV film to give a uniform film of about 100 nm thick. The structures were placed on top of a mask, permitting the deposition of aluminium or calcium on the coated film surface inside a metal evaporator. Metal layers were of typically 500-1000 Å in thickness. Metal contacts were then attached to the electrodes and connected to a DC source. The active device area was typically 4 mm^2.

The bilayer device (ITO/PPV/PDB-PPV/Ca) shows maximum efficiency 1.5 % with luminance in excess of 4,500 cd/m^2 with turn-on voltage at 9V. A bilayer device was also constructed with PVK as the hole-transporting layer produced a maximum efficiency of 0.6% with Al cathodes.

EXAMPLE 4 Preparation of the model oligomer **9**



7 **8** **9**

pale green crystals, m.p. 80-81 °C
λ_{max} ($CHCl_3$) 362 nm, (film) 366 nm
blue-green fluorescence, PL_{max} (film) 2.6 eV

Figure 5 Preparation of dialkoxy-substituted oligomer **9**

A mixture of the 2,3-dimethoxybenzaldehyde **7** (0.33 g, 2.0 mmol) and 1,4-[(2,3-dibutoxy)xylylene]-bis(diethylphosphonate) **8** (0.52 g, 1.0 mmol) in toluene (10 cm^3) was stirred and heated to *ca.* 100 °C under an atmosphere of nitrogen. Potassium tert-butoxide (0.35 g, 3.0 mmol) was added all at once into the hot mixture resulting in a colour change to orange-brown. The mixture was then heated to reflux for 4 h. After allowing to cool to room temperature, toluene was added (20 cm^3) followed by hydrolysis with acetic acid (10% aq, 20 cm^3). The organic layer was separated, washed with water until the organic layer was tested neutral. The organic fraction was then dried, followed by removal of the solvent under reduced pressure to yield a yellow oil. The product **9** was isolated by column chromatography (99:1 hexane:diethyl ether v/v) and further purified by recrystallisation from methanol to give greenish-white needles (0.35 g, 64 %). m.p. 80.0-81.0 °C; δ_H(250MHz; $CDCl_3$) 7.49-7.47 (6H, m, Ar-*H* & C*H*=C*H*), 7.30-7.26 (2H, m, ArH_a), 7.08 (2H, t, *J* 8.0, ArH_b), 6.86-6.83 (2H, m, ArH_c), 4.04 (4H, t, *J* 6.6, ArOCH_2), 3.89-3.87 (12H, m, ArOCH_3), 1.88-1.77 (4H, m, CH_2), 1.64-1.49 (4H, m, CH_2), 1.00 (6H, t, *J* 7.2, CH_3); δ_C(63.5 MHz; $CDCl_3$) 153.1 (C, Ar), 150.6 (C, Ar), 147.1 (C, Ar), 132.0 (C, Ar), 131.7 (C,

Ar), 124.2 (CH, Ar), 124.1 (CH, Ar), 123.4 (CH, Ar), 121.0 (CH, Ar), 117.9 (CH, Ar), 111.3 (CH, Ar), 73.7 (OCH_2), 61.1 (OCH_2), 55.8 (OCH_2), 32.4 (CH_2), 19.4 (CH_2), 14.0 (CH_3); *m/z* (CI) 547 (MH^+, 75 %), 402 (10), 166 (40), 72 (C_4H_8O, 60), 52 (C_4H_4, 70); Found (MH^+) 547.3060; $C_{34}H_{42}O_6$ requires 546.2981; (Found: C, 74.7; H, 7.8; $C_{34}H_{42}O_6$ requires C, 74.7; H, 7.8 %); λ_{max} ($CHCl_3$/nm) 366; λ_{max} (film/nm) 362; PL_{max} (film/nm) 477; PL efficiency (solid state) *ca.* 80%.

X-ray structure of **9**

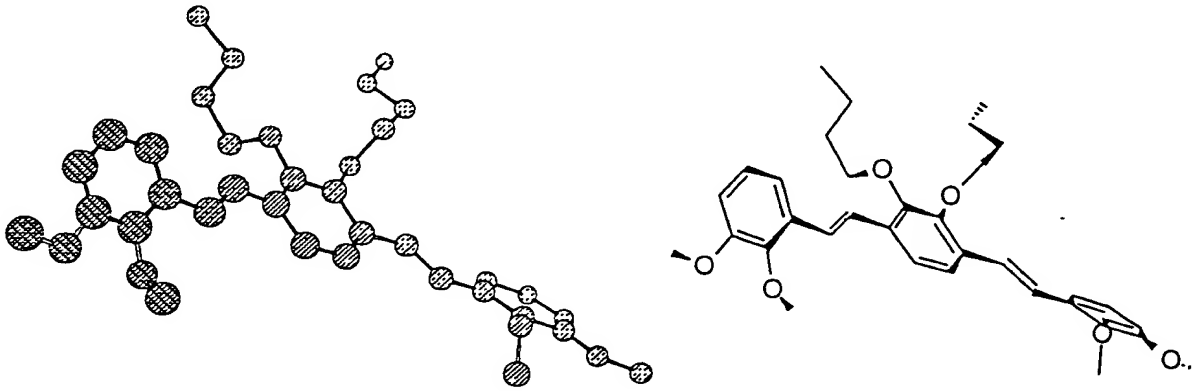
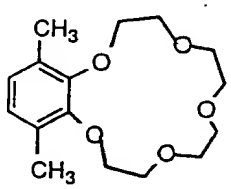


Figure 6 The X-ray crystal structure of oligomer **9**

The *X*-ray of the oligomer **9** shows an unusual cisoid-like conformation around the *trans*-vinylene bond (Figure 6). The benzene rings are twisted out of the plane of the vinylene linkage by about 15° and the benzene rings in turn are twisted at a 30° angle from one another in a regular pattern. This twist will eventually cause an interruption in the polymer backbone conjugation after every 4 benzene rings. The oligomer shows high PL efficiency (*ca.* 80±8 %) in the solid state.

Synthesis of Monomers



14

3,6-Dimethylbenzo-15-crown-5

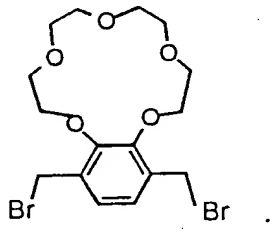
To a solution of dimethyl catechol **4** (2.5 g, 18 mmol) in tetrahydrofuran (100 cm^3) under a nitrogen atmosphere was added sodium hydroxide (1.44 g, 36 mmol). The mixture was left stirring for an hour and a solution of tetraethyleneglycol-di-*p*-tosylate (9.05 g, 18 mmol) in tetrahydrofuran (50 cm^3) was added in dropwise over 30 min. The mixture was refluxed for 22 h. The mixture was cooled, the solvent removed and the residue taken up in dichloromethane (200 cm^3). The organic layer was extracted with water (3 x 100 cm^3) and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield a brown crude. The benzo crown ether was isolated by flash column chromatography (hexane followed by 9:1 hexane:ethyl acetate v/v) to yield the ether **14** as a colourless oil (2.2 g, 41 %). R_f 0..25 (6:4 hexane:ethyl acetate v/v);

ν_{max} (KBr)/cm^{-1} 2860, 1580, 1491 (Ar), 1281, 1134, 1081 (C-O);

δ_H(400 MHz; $CDCl_3$) 6.79 (2H, s, Ar-*H*), 4.11 (2 x 2H, t, *J* 5.2, Ar-OCH_2), 3.96 (2 x 2H, t, *J* 5.2, ArO-CH_2CH_2), 3.74 (4 x 2H, m, OCH_2), 2.22 (6H, s, $ArCH_3$);

δ_C(400 MHz; $CDCl_3$) 150.6 (C, Ar), 150.6 (C, Ar), 129.8 (C, Ar), 129.8 (C, Ar), 125.4 (CH, Ar), 125.4 (CH, Ar), 71.9 (CH_2), 71.9 (CH_2), 71.1 (CH_2), 71.1 (CH_2), 70.6 (CH_2), 70.6 (CH_2), 70.3 (CH_2), 70.3 (CH_2), 15.8 (CH_3), 15.8 (CH_3);

m/z (CI) 297 (MH^+, 20 %), 244 (5), 164 (10); Found (MH^+) 297.1702; $C_{16}H_{24}O_5$ requires 296.1624; (Found: C, 64.4; H, 8.1; $C_{16}H_{24}O_5$ requires C, 64.8; H, 8.2 %).

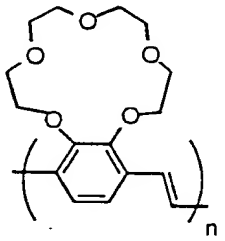


10

3,6-Bis(bromomethyl)-benzo-15-crown-5 **10**

A mixture of the benzo-crown ether **14** (1.77 g, 5.97 mmol), *N*-bromosuccinimide (2.18 g, 12.2 mmol) and benzoyl peroxide (0.14 g, 0.6 mmol) in carbon tetrachloride (50 cm^3) was heated to reflux for 5 h after which the succinimide had floated to the surface of the

solvent mixture. After allowing to cool to room temperature, the mixture was filtered through Celite© and washed with ether. The filtrate was collected and the solvent removed under reduced pressure. The residue was taken up in ether (100 cm^3) and the organic layer extracted with water (2 x 50 cm^3). The organic fraction was dried over $MgSO_4$ and the solvent removed under reduced pressure to produce the crude product as an orange-coloured solid. Recrystallisation from boiling hexane yielded the bis bromomethyl product **10** as a colourless solid **10** (0.56 g, 21 %). m.p. 127.5-128.5 °C; R_f 0.32 (6:4 hexane:ethyl acetate v/v);
ν_{max} (neat)/cm^{-1} 2875, 1451 (Ar), 1287, 1146, 1057 (C-O), 677 (C-Br);
δ_H(250 MHz; $CDCl_3$) 7.09 (2H, s, Ar-*H*), 4.53 (4H, s, CH_2Br), 4.33 (4H, t, *J* 5.0, $ArOCH_2$), 4.00 (4H, t, *J* 5.0, $ArOCH_2CH_2$), 3.75 (8H, m, OCH_2);
δ_C(100 MHz; $CDCl_3$) 150.9 (C, Ar), 150.9 (C, Ar), 133.4 (C, Ar), 133.4 (C, Ar), 126.1 (CH, Ar), 126.1 (CH, Ar), 72.6 (CH_2), 72.6 (CH_2), 71.1 (CH_2), 71.1 (CH_2), 70.7 (CH_2), 70.7 (CH_2), 70.4 (CH_2), 70.4 (CH_2), 27.7 (CH_2), 27.7 (CH_2);
m/z (CI) 470 ($M+NH_4^+$, 58 %), 390 (5), 312 (12), 44 (15); Found ($M+NH_4^+$) 470.0178; $C_{16}H_{22}O_5Br_2$ requires 451.9835; (Found: C, 42.5; H, 4.8; Br, 35.2 $C_{16}H_{22}O_5Br_2$ requires C, 42.5; H, 4.9; Br, 34.9 %).



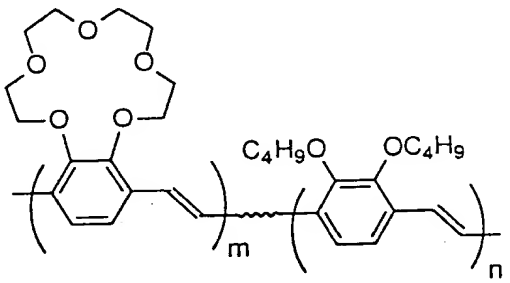
2

15C5-PPV **2**

A degassed solution of KO^tBu (0.1 g, 0.88 mmol) in dry THF (16 cm^3) was added slowly over 20 min to a degassed solution of the dibromide monomer **10** (0.2 g, 0.44 mmol) in dry THF (16 cm^3) at room temperature. The reaction mixture was stirred at ambient temperature under nitrogen for 18 h, after which it was poured into methanol (600 cm^3) with stirring. The resultant yellow precipitate was collected, washed with methanol and dried *in vacuo*. The polymer was redissolved in minimum $CHCl_3$ and reprecipitated into methanol

(600 cm^3). The solid was collected through filtration and dried *in vacuo* to afford the polymer **9** as an orange solid (75 mg, 58 %).
ν_{max} (film)/cm^{-1} 2925, 2867, 1492 (Ar), 1285, 1133 (C-O), 938 (*trans*-vinylene);
δ_H(400 MHz; $CDCl_3$) 7.50-7.25 (2H, br m, conjugated unit), 4.25 (4H, br m, $ArOCH_2$), 4.05 (4H, br m, $ArOCH_2CH_2$), 3.80 (8H, br m, OCH_2);
δ_C(100 MHz; $CDCl_3$) 150.5, 131.5, 121.0 (C, conjugated aromatic carbons), 71.5, 70.5, 70.5 (crown ether CH_2) (conjugated units not visible using 8,000 scans);
Found: C, 62.6; H, 6.8; Br, 1.4; $[C_{16}H_{20}O_5]_n$ requires C, 65.7; H, 6.9; Br, 0 %). GPC assay in $CHCl_3$ revealed M_W 10.7 x 10^6, M_n 126 x 10^3 and M_W/M_n 84; $l_{max}(CHCl_3)$/nm 436; l_{max}(film)/nm 442.

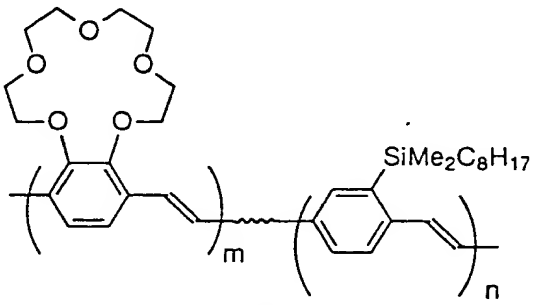
Synthesis of Copolymers



12

15C5-DB PPV copolymer **12**
A degassed solution of KO^tBu (0.26 g, 2.2 mmol) in dry THF (40 cm^3) was added slowly over 20 min to a degassed solution of a mixture of monomers, bis(bromomethyl)-benzo-15-crown-5 monomer **10** (0.2 g, 0.44 mmol) and 2,3-dibutoxy-1,4-bis(bromomethyl) benzene **6** (0.18 g, 0.44 mmol) in dry THF (40 cm^3) at room temperature. The reaction mixture was left stirring at ambient temperature under nitrogen for 6 h, and poured into methanol (500 cm^3) with stirring. The resultant orange precipitate was collected, washed with methanol and dried *in vacuo*. The polymer was redissolved in minimum $CHCl_3$ and reprecipitated into methanol (500 cm^3). The solid was collected through filtration and dried *in vacuo* to afford the polymer as a bright orange solid (0.15 g, 35 %).
ν_{max} (film)/cm^{-1} 2956, 2869, 1436 (Ar), 1283, 1135 (C-O), 974 (*trans*-vinylene);

δ_H(400 MHz; $CDCl_3$) 7.49-7.45 (H-conjugated units), 4.22-3.73 (20H m, br, OCH_2 & $ArOCH_2$), 1.84-1.57 (8H, m, br, CH_2), 1.03-0.99 (6H, m, br, CH_3); *m*:*n* ratio determined by ^1H NMR to be approximately 1:1;
Found: C, 70.0; H, 7.8; Br, 0.9; $[C_{32}H_{42}O_7]_n$ requires C, 71.4; H, 7.8; Br, 0 %;
GPC assay in $CHCl_3$ revealed M_w 2.7 x 10^6 M_n 24 x 10^3 and M_w/M_n 110; $\lambda_{max}(CHCl_3)$/nm 442; λ_{max}(film)/nm 452.



13

15C5-DMOS PPV copolymer **13**

A degassed solution of KO^tBu (0.16 g, 1.3 mmol) in dry THF (12 cm^3) was added slowly over 20 min to a degassed solution of a mixture of monomers, **10** (0.14 g, 0.3 mmol) and 2-methyloctylsilyl-1,4-bis(bromomethyl) benzene **11** (0.13 g, 0.3 mmol) in dry THF (13 cm^3) at room temperature. The reaction mixture was left stirring at ambient temperature under nitrogen for 8 h, after which it was poured into methanol (200 cm^3) with stirring. The resultant orange precipitate was collected, washed with methanol and dried *in vacuo*. The polymer was redissolved in minimum $CHCl_3$ and reprecipitated into methanol (200 cm^3). The solid was collected through filtration and dried *in vacuo* to afford the polymer as a bright orange solid (0.13 g, 76 %).
ν_{max} (film)/cm^{-1} 2923, 2856, 1459 (Ar), 1283, 1137 (C-O), 937 (*trans*-vinylene);
δ_H(400 MHz; $CDCl_3$) 7.67-6.95 (9H, m, br, H-conjugated units), 4.22 (4H, s, br, $ArOCH_2$), 4.05 (4H, s, br, $ArOCH_2CH_2$), 3.79 (8H, s, br, OCH_2), 1.31-1.22 (12H, m, br, CH_2), 0.88 (5H, m, br, CH_2CH_3), 0.43-0.36 (6H, m, br, CH_3); *m*:*n* ratio determined by ^1H NMR to be approximately 1:1;
Found: C, 71.4; H, 8.3; Br, 1.9; $[C_{34}H_{48}O_5Si]_n$ requires C, 72.3; H, 8.6; Br, 0 %;

GPC assay in $CHCl_3$ revealed M_w 286 x 10^3 M_n 37 x 10^3 and M_w/M_n 7.7; $\lambda_{max}(CHCl_3)$/nm 434; l_{max}(film)/nm 442.

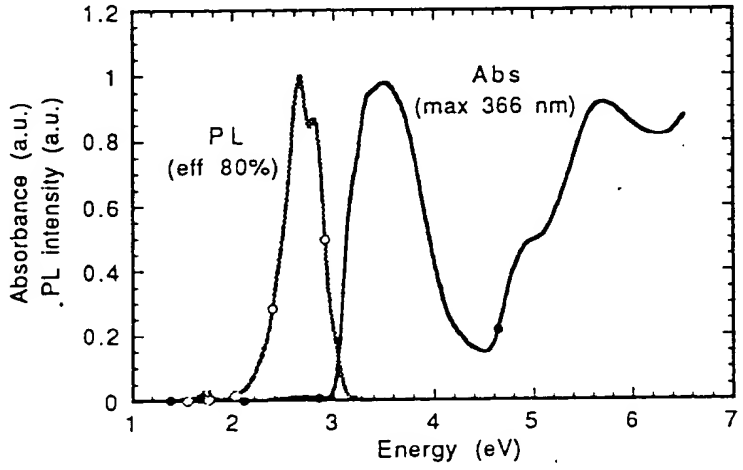


Figure 7 Absorption and PL spectra of films of oligomer **9**

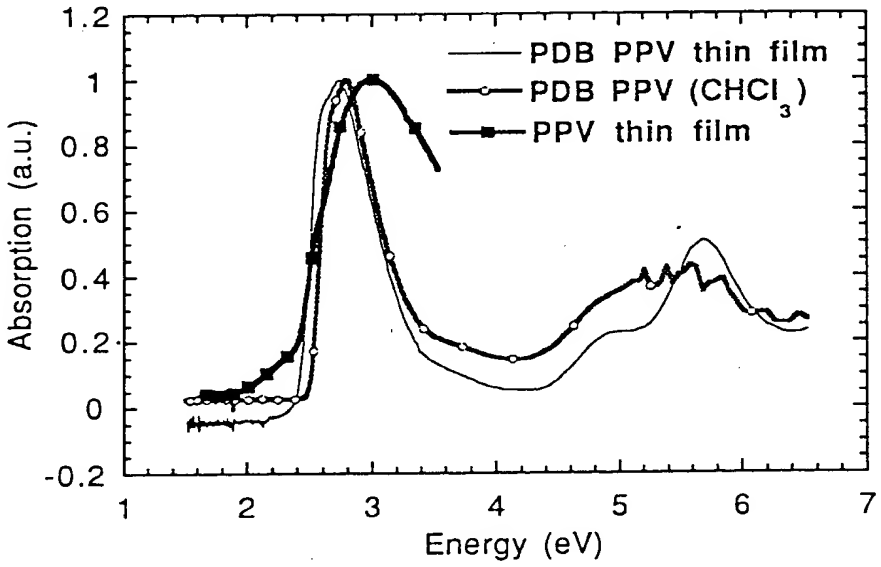


Figure 8 Absorption spectra of PDB PPV **1** compared with PPV film

GPC assay in $CHCl_3$ revealed M_w 286 x 10^3 M_n 37 x 10^3 and M_w/M_n $\lambda_{max}(CHCl_3)$/nm 434; l_{max}(film)/nm 442.

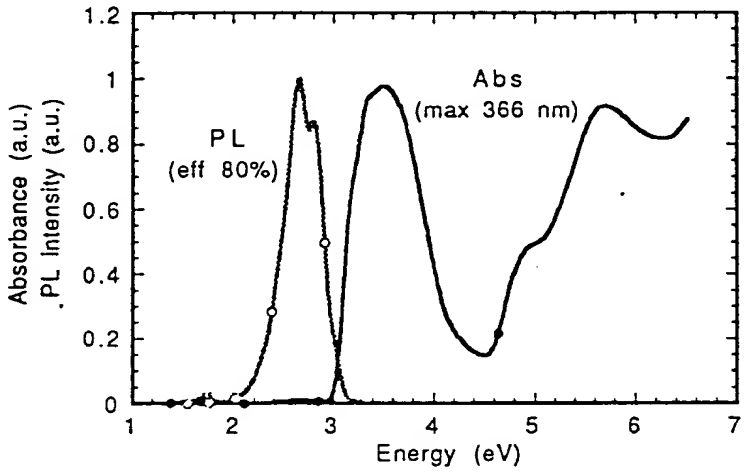


Figure 7 Absorption and PL spectra of films of oligomer **9**

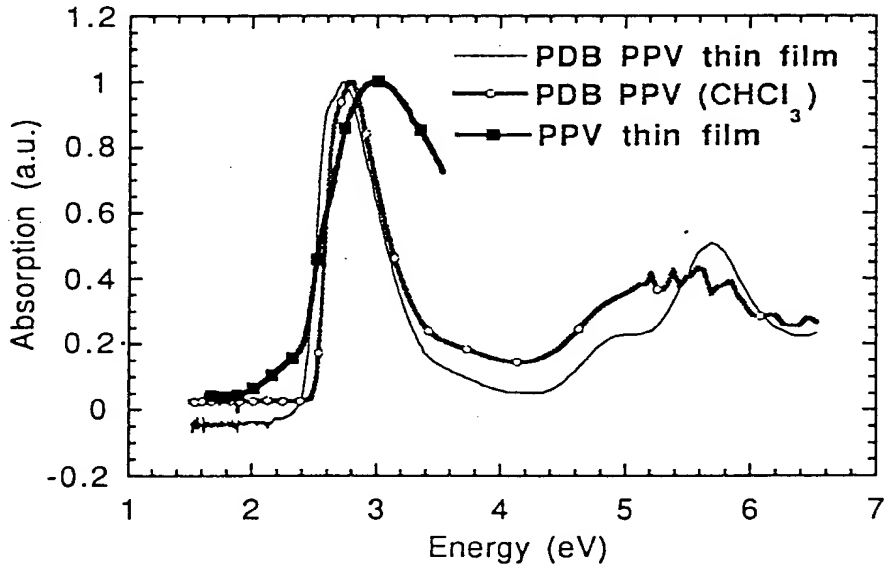


Figure 8 Absorption spectra of PDB PPV **1** compared with PPV film

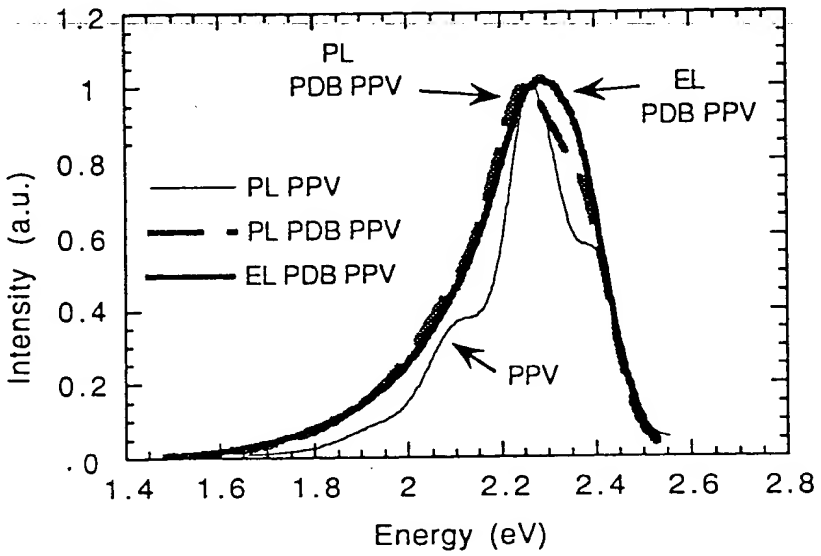


Figure 9 PL spectra of PDB PPV **1** compared with PPV film and EL spectra of a bilayer device (configuration ITO/PPV/PDB-PPV **1**/Ca)

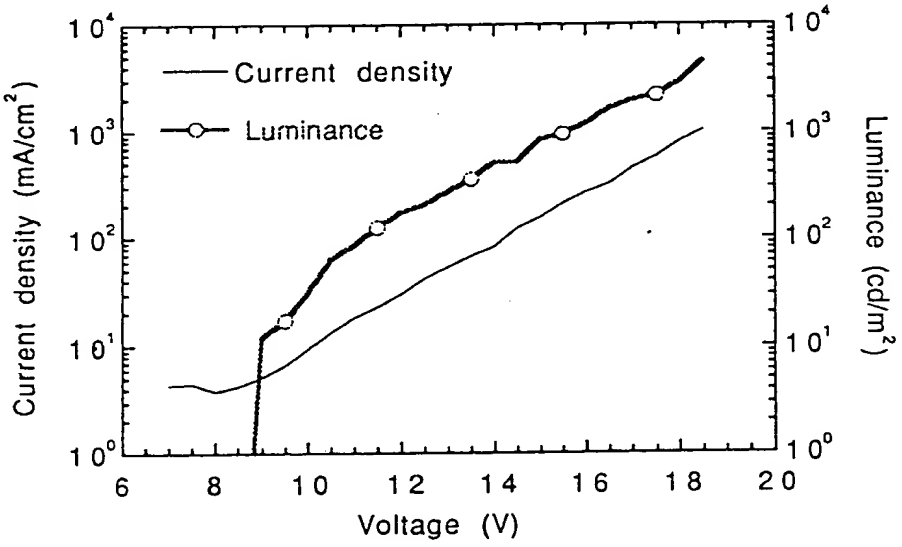


Figure 10 Plot of current density vs applied voltage for a bilayer device (configuration ITO/PPV/PDB-PPV/Ca)

Table 1 Summary of efficiency data for the polymers **12** and **13** in comparison with DMOS-PPV and DB-PPV **1**

Polymer	PL efficiency[a] (%)	EL internal quantum efficiency[b] (Cd/A)

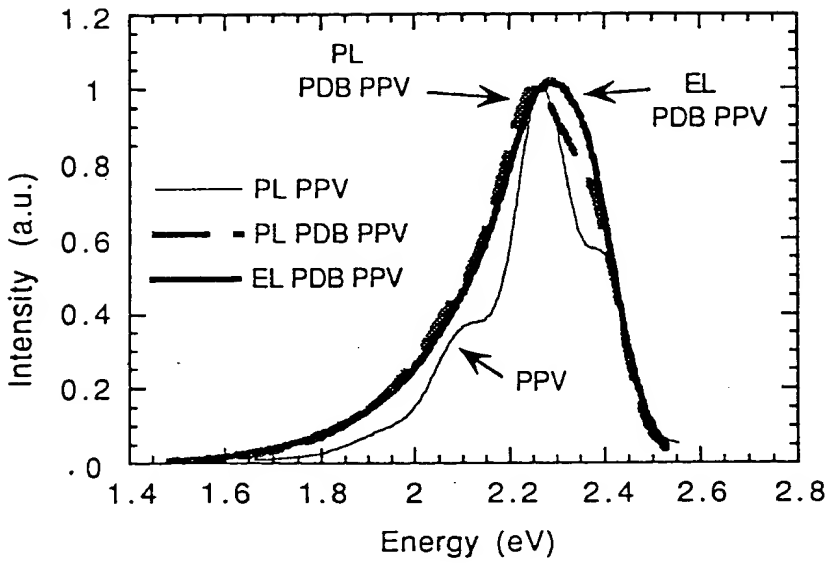


Figure 9 PL spectra of PDB PPV **1** compared with PPV film and EL spectra of a bilayer device (configuration ITO/PPV/PDB-PPV **1**/Ca)

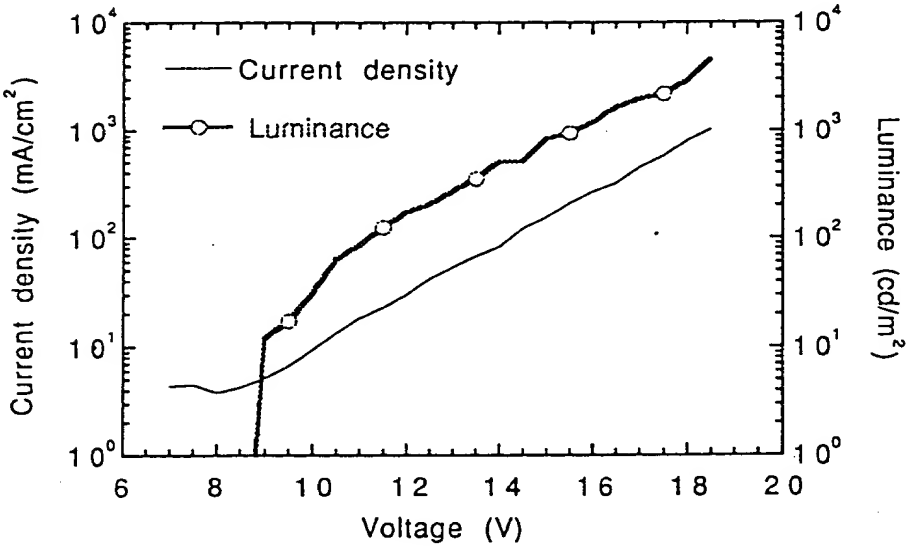


Figure 10 Plot of current density vs applied voltage for a bilayer device (configuration ITO/PPV/PDB-PPV/Ca)

Table 1 Summary of efficiency data for the polymers **12** and **13** in comparison with DMOS-PPV and DB-PPV **1**

Polymer	PL efficiency[a] (%)	EL internal quantum efficiency[b] (Cd/A)

15C5-DB PPV **11**	38	0.35
15C5-DMOS PPV **13**	48	0.3
DMOS-PPV	60	not available
DB-PPV **1**	40	0.015

[a] Measurements made on films; [b] Measurements on ITO/polymer/Al devices, thickness between 100-200 nm.

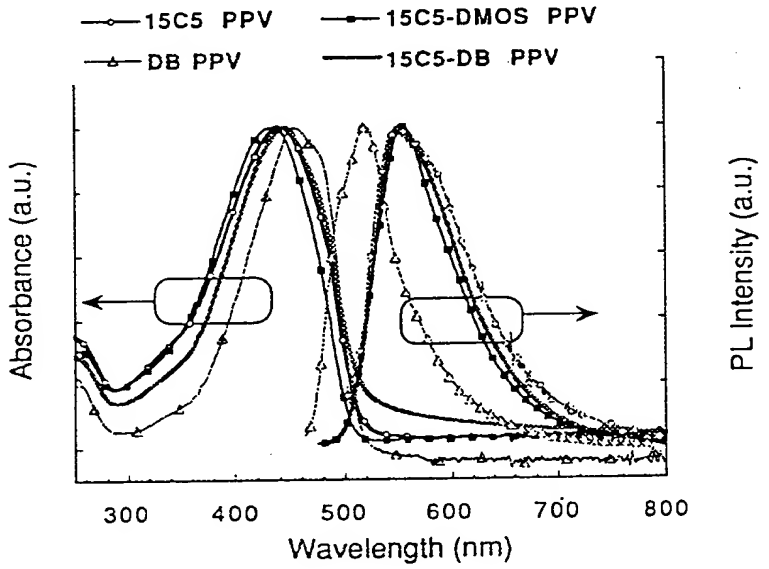


Figure 11 Absorption and photoluminescence spectra of films of copolymers **12** and **13**

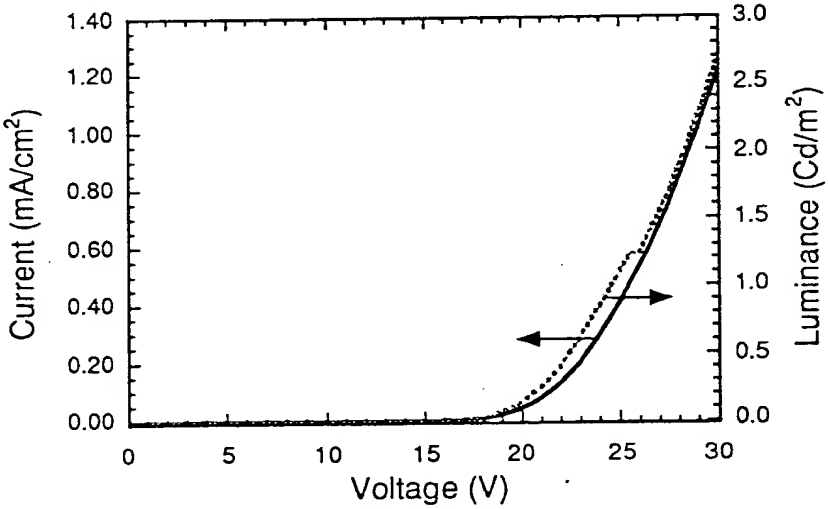
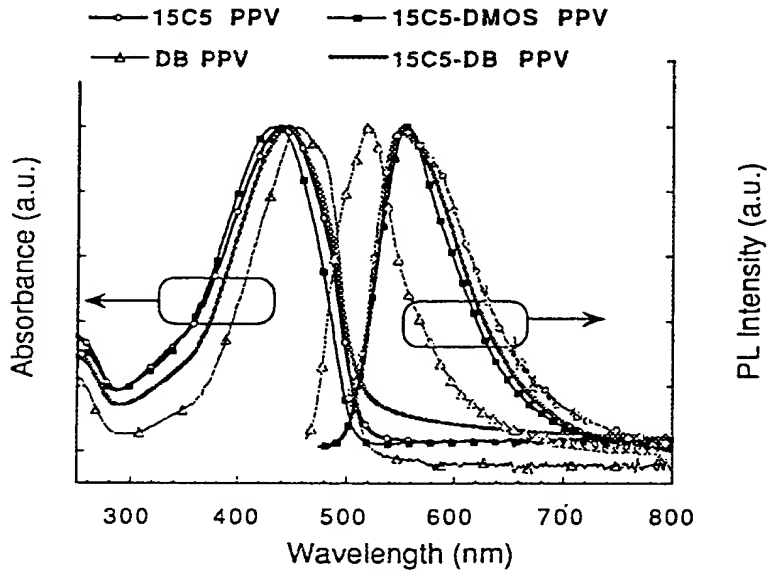


Figure 12 I-V-L plots for single layer device ITO/15C5-DB PPV **12**/Al

15C5-DB PPV **11**	38	0.35
15C5-DMOS PPV **13**	48	0.3
DMOS-PPV	60	not available
DB-PPV **1**	40	0.015

[a] Measurements made on films; [b] Measurements on ITO/polymer/Al devices, thickness between 100-200 nm.



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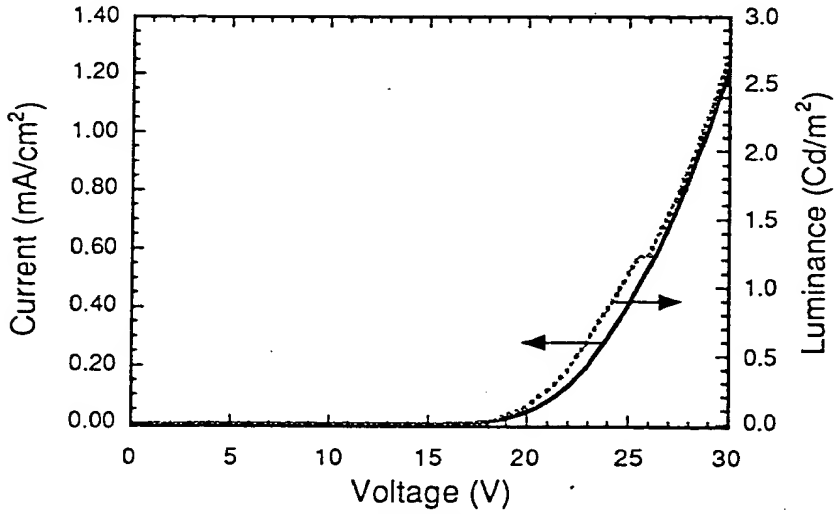

Figure 12 I-V-L plots for single layer device ITO/15C5-DB PPV **12**/Al

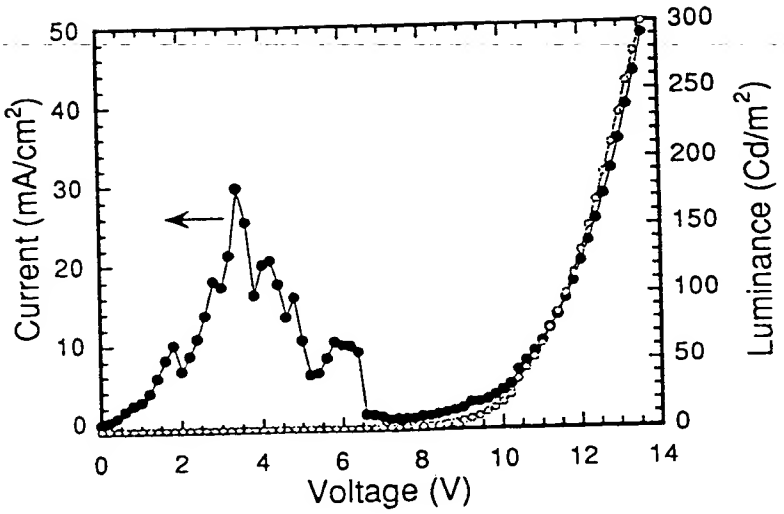

Figure 13 I-V-L plots for single layer device ITO/15C5-DMOS PPV13/Al

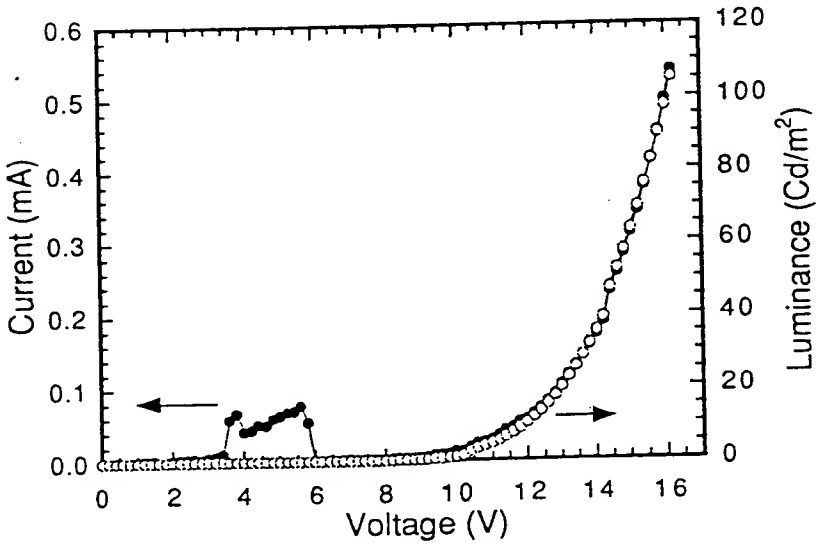

Figure 14 I-V-L plots for double layer device ITO/PPV/15C5-DMOS PPV13/Al
At drive voltages *ca.* 14 V, EL quantum efficiency up to 2.0%

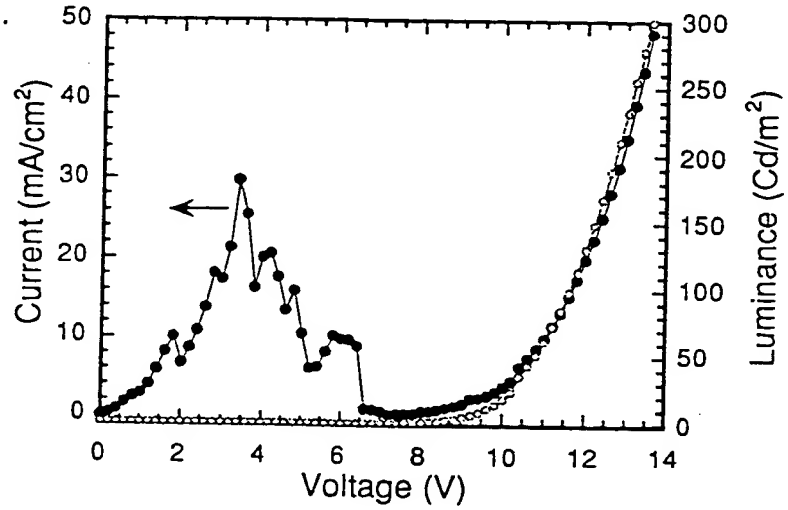

Figure 13 I-V-L plots for single layer device ITO/15C5-DMOS PPV13/Al

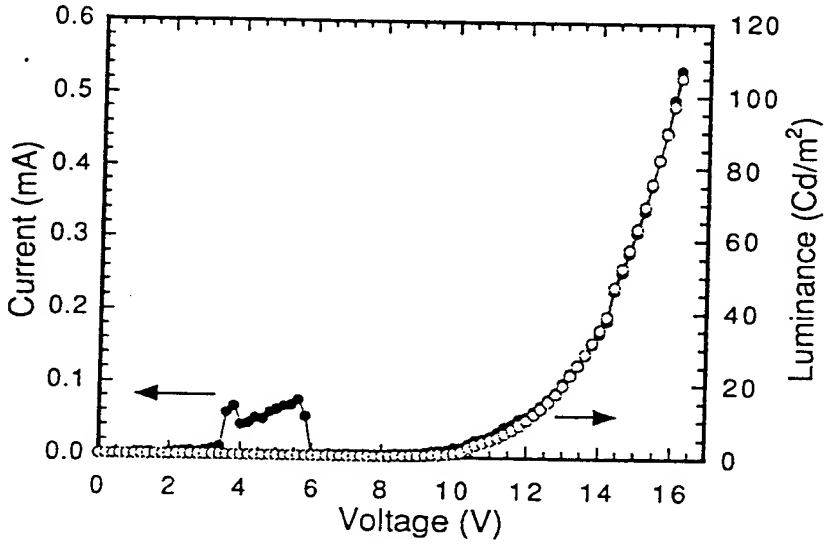

Figure 14 I-V-L plots for double layer device ITO/PPV/15C5-DMOS PPV13/Al
At drive voltages *ca.* 14 V, EL quantum efficiency up to 2.0%

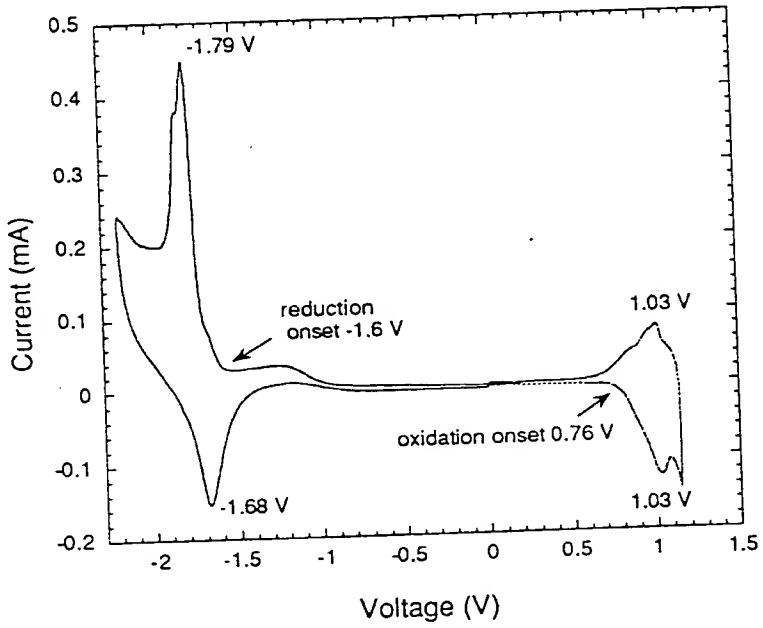

Figure 15 CV plot of 15C5-DB PPV copolymer 12

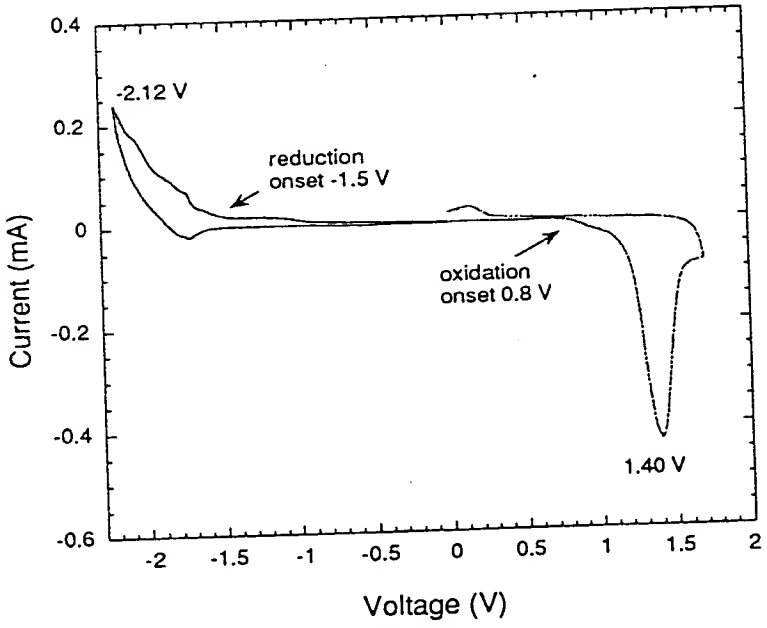

Figure 16 CV plot of 15C5-DMOS PPV copolymer 13

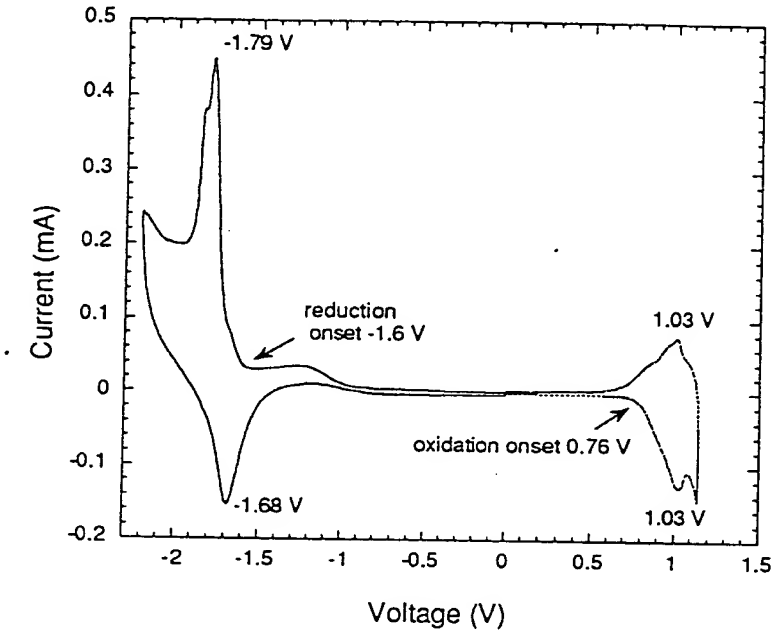

Figure 15 CV plot of 15C5-DB PPV copolymer **12**

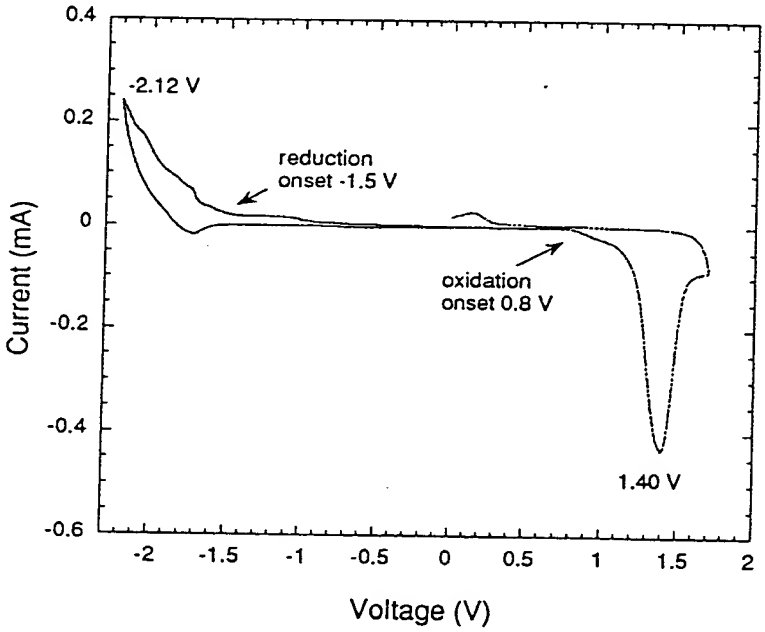

Figure **16** CV plot of 15C5-DMOS PPV copolymer **13**